The Catalytic Activity of α-AlF$_3$/Al$_2$O$_3$ and β-AlF$_3$/Al$_2$O$_3$

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The properties of a series of α-AlF$_3$/Al$_2$O$_3$ and β-AlF$_3$/Al$_2$O$_3$ catalysts were investigated. The ratio of the number of Lewis and Brønsted acid sites is important for the catalytic behaviour in the double-bond isomerization of 1-pentene. It was found that both the catalytic activity and the effective acidity (acidity per unit of surface area and per fluorine atom) is larger for β-AlF$_3$/Al$_2$O$_3$ than for α-AlF$_3$/Al$_2$O$_3$ catalysts. In the β-AlF$_3$/Al$_2$O$_3$ catalysts the size of the AlF$_3$ crystallites is smaller, whereas the total AlF$_3$ surface area is larger than in the α-AlF$_3$/Al$_2$O$_3$ catalysts. When it is assumed that catalytic activity is located at the boundary of AlF$_3$ crystallites and Al$_2$O$_3$, the difference in catalytic behaviour between α-AlF$_3$/Al$_2$O$_3$ and β-AlF$_3$/Al$_2$O$_3$ can be explained on account of the difference in size of the AlF$_3$ crystallites.

INTRODUCTION

In the last decade several investigations have been reported concerning the influence of fluorine on the activity of Al$_2$O$_3$-supported catalysts. Besides investigations with respect to fluorinated alumina (1–11) attention was also paid to the catalytic activity of AlF$_3$ (12, 13, 14). Until 1965 only one modification of AlF$_3$, *viz.*, the α-modification, was reported. In 1965 a new AlF$_3$ modification was described (15) by Christoph *et al.*, *viz.*, the metastable β-AlF$_3$ form, which proved to be more active than α-AlF$_3$ in the hydrofluorination of acetylene. The metastable β-modification is transformed irreversibly into the stable α-form at temperatures higher than approximately 550°C.

In 1966 Shinn *et al.* (16) described the preparation of a material which they called a γ-modification of AlF$_3$ with a tetragonal structure. The correctness of their conclusion was, however, doubted by Baumer *et al.* (17). In a patent application of Toyo Rayon (18) also three AlF$_3$ modifications are distinguished. Apart from a restricted X-ray pattern, further data about the AlF$_3$(III) modification are lacking. It is, however, clearly demonstrated in this patent application and in a later investigation (19) that combinations of β-AlF$_3$ and Al$_2$O$_3$ possess a much more pronounced catalytic activity than combinations of α-AlF$_3$ and Al$_2$O$_3$ in several cracking and disproportionation reactions.

In this paper the catalytic activity of a series of α-AlF$_3$/Al$_2$O$_3$ and β-AlF$_3$/Al$_2$O$_3$ catalysts in the isomerization of 1-pentene is described and related to acidity and sur-

TABLE 1

CHARACTERISTICS OF α- AND β-ALUMINUM FLUORIDE[a]

	α-AlF$_3$	β-AlF$_3$
Crystal system	Rhombic	Hexagonal
Space group	D$_3^7$–R$_{32}$	D$_{6h}^4$–P6/mmc
Unit cell parameters	a = 0.4927 nm c = 1.2445 nm	a = 0.693 nm c = 0.7125 nm
Molecules AlF$_3$ per unit cell	6	6
Unit cell volume	2.615 (nm)^3	2.964 (nm)^3
Calculated density	3.197 g/cm^3	2.815 g/cm^3

[a] According to Christoph *et al.* (15).

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face area of the catalysts and to the size of the AlF_3 crystallites.

EXPERIMENTAL

Catalysts

The β-AlF_3/Al_2O_3 catalysts were prepared according to the method previously described (19, 20). An excess of gibbsite ($Al_2O_3 \cdot 3H_2O$), activated at 300°C, is heated with an aqueous ammoniacal solution of NH_4F in a closed reaction vessel at 100°C during 30 min. $(NH_4)_3AlF_6$ is precipitated in the pores of the gibbsite, thus forming an intimate mixture with Al_2O_3, which is transformed into a mixture of β-AlF_3 and Al_2O_3 by calcination at 450°–500°C. By regulating the excess of gibbsite it is possible to prepare catalysts with any desired composition of β-AlF_3 and Al_2O_3.

The α-AlF_3/Al_2O_3 catalysts were prepared from the β-AlF_3/Al_2O_3 catalysts by calcination at 570°C during 16 hr in a stream of dry air; X-ray diffraction with Ni-filtered Cu K_α-radiation was used to verify the completeness of the transformations of β-AlF_3 into the α-form.

In all experiments the 100–400 mesh catalyst fraction was used. The fluorine contents of the catalysts were determined by activation analysis (measurement of the ^{18}F activity caused by the reaction $^{19}F (n, 2n)\,^{18}F, T_{1/2} = 110$ min).[*]

Surface areas of the catalysts were determined in a Carlo Erba sorptometer by nitrogen adsorption (BET-method).

Acidity Titration

Catalyst acidity measurements were performed by titration with n-butylamine (in benzene) at room temperature, using a series of Hammett indicators (Ho acidity) and arylmethanol indicators (Hr acidity) (21, 22), mentioned in Table 3. The indicators d,g,h,j, and k were commercially available and were used without further purification. The other indicators were prepared according to the methods described in

* Measurements carried out by the Reactor Centrum Nederland in Petten, The Netherlands.

the cited references; their structures were confirmed with infrared and NMR spectrometry and ultimate analysis.

Prior to the acidity titrations the catalyst was calcined at 400°C in a stream of dry air for 16 hr and subsequently in a stream of dry nitrogen for 1 hr. Both gases were dried with molecular sieve 3A. In one experiment the catalyst was immersed in water for 1 hr; after filtration and 3 hr of drying in vacuum at 110°C, the catalyst was treated as described above. Weighed amounts of approximately 0.1 g of catalyst were transferred into screw-cap bottles supplied with a septum and covered with 2 ml of dry benzene; a few drops of an indicator solution (0.1 M in benzene) were added to each bottle. These operations were performed in a dry nitrogen box. To attain rapid equilibrium, the titrations with n-butylamine in benzene were executed in an ultrasonic bath, as described previously by Bertolacini (23). The catalyst acidity was in all cases determined in duplicate; the maximum difference amounted to approx. 0.02 mEq/g.

Catalytic Activity

Double-bond isomerization of 1-pentene was selected as a model reaction. The 1-pentene was commercially available and was used as received. The investigations were carried out in a fixed bed stainless steel reactor heated by means of a fluidized bed furnace. The catalyst (1 g) was activated *in situ* at 450°C with dry air (16 hr) and dry helium (1 hr). After cooling to the reaction temperature (150°C in most cases) a helium stream, saturated at 0°C with 1-pentene, was passed continuously through the reactor at a total pressure of approx. 1 atm. Gas flow, temperature and pressure were regulated with conventional devices. Air and helium were dried over molecular sieve 3A, helium being freed from traces of oxygen by a hydrogenated copper catalyst. To study the influence of water on catalyst activity at reaction conditions, it was possible to inject small pulses of H_2O into the reactant stream. Periodically the effluent stream was sampled and analyzed in a Hewlett Packard 700 gas chromatograph

equipped with a flame ionization detector. Separation of the products was performed at room temperature on a $10 \, \text{m} \times \frac{1}{4}$ inch column packed with 15% Apiezon L on Chromosorb DMCS, 60–80 mesh. *Cis-* and *trans*-2-pentene were the only reaction products that could be detected. From calculations it is obvious that, under the used conditions, mass transfer limitations to the catalyst as well as diffusion limitations in the pellet do not exist.

RESULTS AND DISCUSSION

Catalyst Properties

The results of analysis of the used α-AlF₃/Al₂O₃ catalysts (A series) and β-AlF₃/Al₂O₃ catalysts (B series) are summarized in Table 2. The BET surface diminishes as more fluorine is incorporated in the catalysts. There exists a difference between the surface areas of the B and the corresponding A catalysts, as a result of the calcination procedure at 570°C during 16 hr causing inter alia transformations in the Al₂O₃ carrier (27). Furthermore, it has been shown that the AlF₃ modification is only visible in the X-ray pattern in the used catalyst samples containing 17% (= 25% AlF₃) or more of fluorine. In a number of publications (3, 7, 28) this phenomenon has also been mentioned, on the understanding that already in catalysts with approximately 6% of fluorine the AlF₃ modification has been observed. In catalysts containing less than 6% of fluorine, the fluorine appears to be restricted to the surface. Apparently, AlF₃ crystallites are formed only in catalysts containing more than 6% of fluorine. In our opinion this explanation holds for the catalysts A₂ and B₃. In A₈ and B₉, however, the presence of AlF₃ crystallites should not be excluded; as a consequence of the specific way of catalyst preparation the crystallites might have been too small or too few in number to be observed in X-ray diffraction.

Acidity Measurements

Table 3 shows the results of the acidity titrations with Ho and Hr indicators. The accuracy of the determinations is approx. 0.01 mEq/g. It clearly follows from Table 3 and the surface area data in Table 2 that the α-AlF₃/Al₂O₃ catalysts contain less acid sites than the β-AlF₃/Al₂O₃ catalysts both on a per gram as well as on a per square metre basis.

One might ascribe this difference in acidity to a deficiency of H₂O as a consequence of the preparation of the α-AlF₃/Al₂O₃ catalysts by calcination during 16 hr, at 570°C. To study this possibility an experiment was performed in which both an α-AlF₃/Al₂O₃ and a β-AlF₃/Al₂O₃ catalyst were immersed for 1 hr in H₂O and the

TABLE 2

PROPERTIES OF THE USED α-AlF₃/Al₂O₃ AND β-AlF₃/Al₂O₃ CATALYST SERIES

Samples	F (wt %)	AlF₃ (wt %)	AlF₃ modification	Surface area (m²/g)
B₃	2.9	(4.2)ᵃ	Not observed	125
B₉	8.9	13.1	Not observed	81
B₁₇	17.0	25.0	β	80
B₂₉	29.2	43.0	β	83
B₃₈	38.4	56.4	β	75
B₄₆	46.2	68.0	β	75
A₂	2.2	(3.3)ᵃ	Not observed	95
A₈	8.2	12.0	Not observed	50
A₁₇	16.7	24.6	α	51
A₃₁	31.1	45.7	α	48
A₄₀	39.8	58.5	α	43
A₄₉	48.5	71.4	α	45

ᵃ Fluorine not present in AlF₃ crystallites.

TABLE 3

ACIDITY MEASUREMENTS ON α-AlF$_3$/Al$_2$O$_3$ (A SAMPLES) AND β-AlF$_3$/Al$_2$O$_3$ (B SAMPLES) BY
n-BUTYLAMINE TITRATION USING ARYLMETHANOL (Hr) AND HAMMETT (Ho) INDICATORS

| | Acidity (mEq/g) | | | | | | | | | |
| | Hr indicators[b] | | | | | Ho indicators[b] | | | | |
Sample	pK$_R$	-11.0[c]	-6.6[d]	-4.0[e]	$+0.8$[f]	pK$_A$	-8.2[g]	-5.6[h]	-3.0[i]	$+1.5$[j]	$+3.2$[k]
B$_3$	0	0.23	0.25	0.24	0	0.23	0.25	0.31	0.32
B$_9$	0	0.18	0.19	0.18	0	0.15	0.16	0.18	0.19
B$_{17}$	0	0.19	0.20	0.19	0	0.14	0.20	0.22	0.22
B$_{29}$	0	0.18	0.18	0.19	0	0.15	0.20	0.21	0.21
B$_{38}$	0	0.16	0.16	0.16	0	0.12	0.15	0.16	0.17
B$_{46}$	0	0.04	0.11	0.14	0	0.04	0.12	0.13	0.14
A$_2$	0	0.15	0.15	0.15	0	0.14	0.16	0.13	0.15
A$_8$	0	0.09	0.09	0.09	0	0.07	0.08	0.08	0.09
A$_{17}$	0	0.07	0.08	0.08	0	0.09	0.07	0.09	0.09
A$_{31}$	0	0.07	0.09	0.08	0	0.06	0.07	0.09	0.08
A$_{40}$	0	0.02	0.04	0.05	0	0.00	0.06	0.07	0.08
A$_{49}$	0	0.00	0.02	0.04	0	0.00	0.03	0.03	0.03
B$_{17}$(H$_2$O)[a]	0	0.14	0.20	0.23	0	0.00	0.19	0.28	0.29
A$_{17}$(H$_2$O)[a]	0	0.08	0.10	0.11	0	0.00	0.10	0.11	0.12

[a] Catalyst samples which had been immersed in water, dried, and calcined (see text).

[b] Hr and Ho indicators with resp. pK$_R$ = -11.0 and pK$_A$ = -8.2 are not converted by the catalyst samples into their acid forms.

[c] 3,3',3''-Trichlorotriphenylmethanol (24).

[d] Triphenylmethanol.

[e] 4,4',4''-Trimethyltriphenylmethanol (25).

[f] 4,4',4''-Trimethoxytriphenylmethanol (5).

[g] Anthraquinone.

[h] Benzalacetophenone.

[i] Dicinnamalacetone (26).

[j] Benzeneazodiphenylamine.

[k] Dimethylyellow.

acidity determined after drying and calcination in the usual way. The results, which are represented in Table 3, show an unambiguous difference in acidity. Therefore it can be concluded that the differences in acidity between B and A catalysts have not been caused by the method of preparation of the latter.

There is a strong similarity between the results of our acidity measurements and those of other investigators. The data of Moerkerken et al. (19) who executed acidity measurements using LiAlH$_4$ as the reactant on a number of β-AlF$_3$/Al$_2$O$_3$ catalysts are qualitatively in agreement with our results. The same holds for the acidity measurements with Ho and Hr indicators of moderate strength on fluorinated alu-
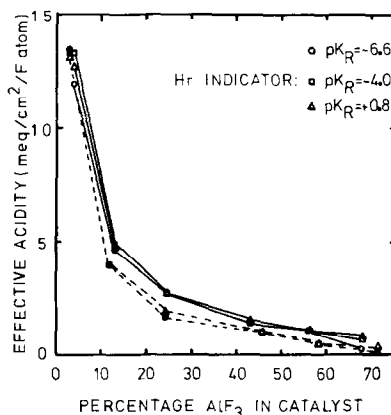

FIG. 1. Effective Hr acidity (acidity per unit of surface area per F atom) of α-AlF$_3$/Al$_2$O$_3$(A) and β-AlF$_3$/Al$_2$O$_3$(B) catalysts. Catalysts A: - - - - -; catalysts B: ———.
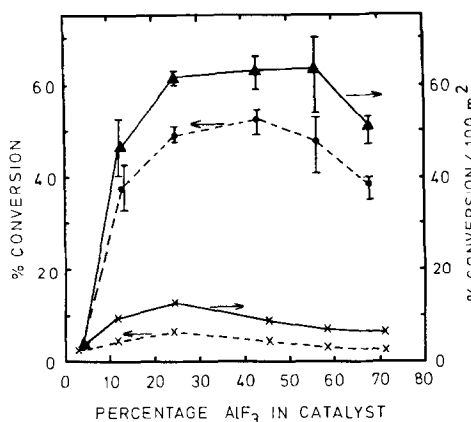
FIG. 2. 1-Pentene conversion after 4 hr of reaction of α-AlF$_3$/Al$_2$O$_3$(A) and β-AlF$_3$/Al$_2$O$_3$(B) catalysts. Catalysts A: ×----×, ×———×; catalysts B: ●----●, ▲———▲ (average of 3 determinations). Conditions: reaction temperature 150°C, WHSV = 2.9 g 1-pentene/g catalyst/hr; % conversion = $\dfrac{\Sigma\ 2\text{-pentene}}{\Sigma\ \text{pentene}} \times 100$.

minas, performed by Covini et al. (5). It is evident that maximum acidity per unit of surface area occurs at intermediate fluorine percentages.

Finally, it is interesting to consider the *effective* acidity (= acidity per unit of surface area and per added fluorine atom). Figure 1, which shows the effective Hr acidity, reveals a difference between the A and B catalyst series, except for the low-fluorinated aluminas (A$_2$,B$_3$). Apparently this difference only exists when AlF$_3$ crystallites are present in the catalysts.

Catalytic Activity

As follows from Fig. 2, the catalytic activity of the B catalysts in the double-bond isomerization of 1-pentene is much

larger than that of the A catalysts, with the exception of the low-fluorinated samples A$_2$ and B$_3$. The pronounced activity of β-AlF$_3$ and of mixtures of β-AlF$_3$ and Al$_2$O$_3$ has been observed by several authors (15, 18, 19); maximum catalytic activity has been observed at intermediate compositions of AlF$_3$ and Al$_2$O$_3$. This can be explained by the pronounced electronegativity of fluorine (incorporated, e.g., during hydrofluorination of Al$_2$O$_3$ according to Fig. 3, step I), which causes an increase in strength of both Lewis acidity (exposed Al atoms) and Brønsted acidity (adsorbed, dissociated, H$_2$O molecules). For the catalytic isomerization of 1-pentene both Lewis and Brønsted sites, which can reversibly change into each other (Fig. 3, step II), are needed; maximum activity is to be expected at intermediate compositions of AlF$_3$ and Al$_2$O$_3$, in which both types of acid sites at present in optimum amounts.

In our experiments none of the used A and B catalysts showed a constant initial activity; it took 2–4 hr before a somewhat constant activity was reached. It is remarkable that the less fluorinated B catalysts suffer a larger decrease in activity than the more fluorinated ones. This is in agreement with data of Gerberich (3) and of Covini (5) and might indicate that the active sites of the catalysts are more stable when larger amounts of fluorine have been incorporated.

The influence of H$_2$O on the catalytic activity of the A and B catalysts was investigated by introducing small pulses of water into the reactant stream during the experiments (see Fig. 4). Figure 4 shows the occurrence, after an initial decrease, of
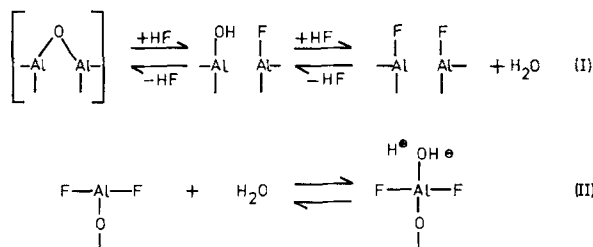

FIG. 3. Formation of Lewis and Brønsted acid sites during the hydrofluorination of alumina.
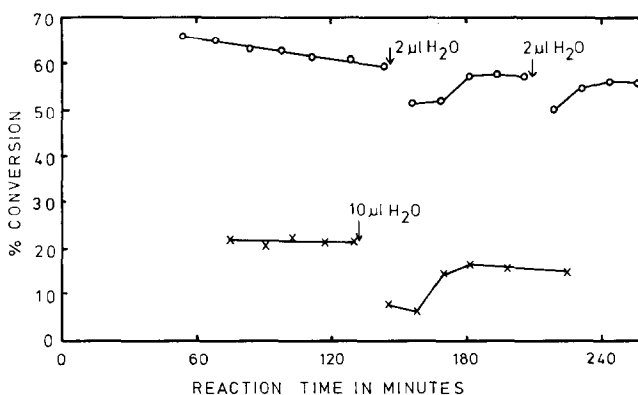
FIG. 4. Influence of H_2O on the catalytic activity of α-AlF$_3$/Al$_2$O$_3$ (A) and β-AlF$_3$/Al$_2$O$_3$ (B). Conditions: O————O, 1 g of B$_{38}$, reaction temperature 150°C, WHSV = 2.9 g 1-pentene/g catalyst/hr; X————X, 3.8 g of A$_{40}$, reaction temperature 170°C, WHSV = 0.5 g 1-pentene/g catalyst/hr; % conversion = $\dfrac{\Sigma \text{ 2-pentene}}{\Sigma \text{ pentene}} \times 100$.

a remarkable recovery of the activity of both catalysts. These results again confirm that the difference in catalytic activity between A and B catalysts is not the consequence of removal of H_2O from the A catalysts owing to the procedure of their preparation.

Product Selectivity

The product selectivity, which is represented as the ratio of *cis-* and *trans*-2-pentene, is in the case of B catalysts in all experiments much larger than the thermodynamic equilibrium value of approximately 0.5. The results, summarized in Fig. 5, clearly show that the cis/trans ratio increases with decreasing conversion. This phenomenon of high cis/trans ratios in the isomerization of *n*-alkenes with acidic catalysts has been reported by several authors (*29, 30, 31*).

Matsuura *et al.* (*30*) relate the results of their experiments with the so-called "acidity composition" (= ratio of Lewis and Brønsted sites) of the catalysts. Catalysts, precalcined at relatively high temperatures, will possess a relatively high L/B ratio, and will show a relatively low catalytic activity and a high cis/trans selectivity; their stability is limited. Catalysts precalcined at relatively low temperatures will possess smaller L/B ratios, a higher cata-

lytic activity and a relatively low cis/trans selectivity; they are more stable. The L/B ratio of a catalyst therefore seems to be of great importance in indicating its catalytic behaviour in double-bond isomerization reactions.

In our experiments the calcination temperature of the catalysts was the same in all cases; however, the Lewis/Brønsted ratio is not only a function of the tempera-
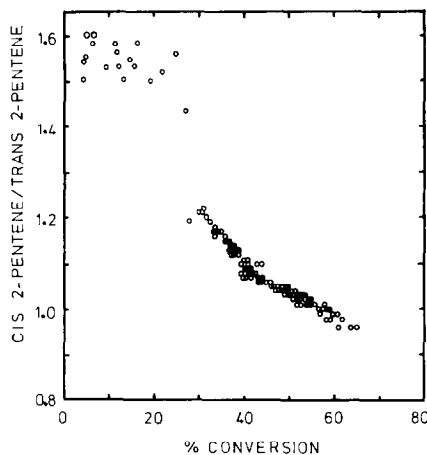

FIG. 5. Product selectivity as a function of conversion with β-AlF$_3$/Al$_2$O$_3$ catalysts. Conditions: reaction temperature 150°C, WHSV = 2.9 g of 1-pentene/g catalyst/hr; % conversion = $\dfrac{\Sigma \text{ 2-pentene}}{\Sigma \text{ pentene}} \times 100$.

ture of pretreatment of the catalysts, but is also determined by the percentage of incorporated fluorine. It can be assumed that catalysts containing small amounts of fluorine will possess a relatively high L/B ratio. The more fluorine is incorporated in the catalysts, the lower their L/B ratio will be; this is a consequence of the fact that Brønsted and Lewis acid sites can be reversibly converted into each other (compare Fig. 3, step II). The acid strength of the Lewis sites will increase when more fluorine is incorporated; this facilitates their conversion into B sites and thus results in a lower L/B ratio. These considerations are supported by experiments of Bulgakov et al. (9), who determined the L/B ratio of fluorinated aluminas by means of infrared spectrometry of adsorbed pyridine, and found that the L/B ratio is indeed related to the fluorine percentage; this ratio becomes smaller when more fluorine is incorporated in the catalyst. Also the results of H₂O-poisoning experiments (see Fig. 4) confirm these suppositions: readsorption of H₂O will result in a smaller L/B ratio (either by the reaction H₂O + L → B, or by the occupation of L sites by H₂O molecules), and the conversion will decrease, as is in accordance with our observations.

Acidity and Activity

No correlation was found between the measured Ho or Hr acidity of the catalysts and their activity, as is obvious from Fig. 2 and Table 3. It should be noticed in this respect that the acidity measurement and the estimation of the catalytic activity have been executed in completely different systems. Moreover, the question arises as to what kind of acidity has been measured with the used Ho and Hr indicators. In the literature there is no unanimity on this subject. It might be possible that only a part of the measured acidity is related to the activity of the catalysts for the double-bond isomerization of 1-pentene.

Activity and Size of AlF₃ Crystallites

The experimental data and results from Fig. 2 show that with the exception of A₂ and B₃ the β-AlF₃/Al₂O₃ catalysts have a

higher activity in the double-bond isomerization of 1-pentene than the corresponding α-AlF₃/Al₂O₃ catalysts, both on a per gram as well as on a per square metre basis. The question arises as to the origin of the remarkable difference in catalytic activity of both groups. From experiments of Moerkerken (19) on the catalytic activity of α- and β-AlF₃ in hexane cracking, it is evident that neither α-AlF₃ nor β-AlF₃ is very active; the carrier Al₂O₃ also shows only a very limited activity. Combinations of Al₂O₃ and β-AlF₃, on the other hand, show a pronounced catalytic activity; this makes it probable that the catalytic activity is located at the boundary surface of the AlF₃ crystallites and the Al₂O₃ carrier. Calculations of AlF₃ crystallite sizes from the width of the reflections in the X-ray pattern show that the AlF₃ crystallite size in the A series (A₁₇–A₄₉) is of the order of 100 nm, and in the B series (B₁₇–B₄₆) of the order of 30 nm. From this and from the greater density of α-AlF₃ with respect to β-AlF₃ (see Table 1) it follows that the transformation of B catalysts into A catalysts is coupled with a considerable increase in AlF₃ crystallite size and a corresponding decrease in the total AlF₃–Al₂O₃ contact area, and therefore in a decrease in catalytic activity. In a recent patent application (32) this conclusion is confirmed: in a number of AlF₃–zeolite catalysts the activity could be directly related to the size of the AlF₃-crystallites: small crystallites promote the catalytic activity.

It is interesting to mention again Covini's article (5), in which a surface rearrangement in the used AlF₃/Al₂O₃ catalyst is reported when the temperature of calcination rises above 550°C. In our opinion this surface rearrangement is brought about by the transformation of β-AlF₃ crystallites into α-AlF₃, which, according to Christoph (15), starts at approximately 550°C.

The difference in catalytic activity between the A and B series is therefore caused by a difference in the extent of the AlF₃–Al₂O₃ contact area. In the low fluorinated aluminas (A₂,B₃), in which the fluorine atoms are located on the surface, there are

no AlF_3 crystallites present. Hence there cannot exist a difference in catalytic activity between A_2 and B_3. The affirmation of this fact by the data in Fig. 2 supports our statement that the difference in catalytic activity of α-AlF_3/Al_2O_3 and β-AlF_3/Al_2O_3 is primarily caused by the difference in AlF_3 crystallite size.

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